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Magnetic anisotropy and geometrical frustration in the Ising spin-chain system $Sr_5Rh_4O_{12}$

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A structural and thermodynamic study of the newly synthesized single crystal $Sr_5Rh_4O_{12}$ is reported. $Sr_5Rh_4O_{12}$ consists of a triangular lattice of spin-chains running along the c-axis. It is antiferromagnetically ordered below 23 K with the intrachain and interchain coupling being ferromagnetic (FM) and antiferromagnetic (AFM), respectively. There is strong evidence for an Ising character in the interaction and geometrical frustration that causes incomplete long-range AFM order. The isothermal magnetization exhibits two steplike transitions leading to a ferrimagnetic state at 2.4 T and a FM state at 4.8 T, respectively. $Sr_5Rh_4O_{12}$ is a unique frustrated spin-chain system ever found in 4d and 5d-based materials without a presence of an incomplete 3d-electron shell. © *2011 American Institute of Physics*. [doi:10.1063/1.3566076]

Quasi-one-dimensional structures combined with geometrical frustration frequently give rise to complex excitations and novel magnetic order. Such behavior is manifested in Co-based compounds such as $CsCoCl_3$,[1] $Ca_3Co_2O_6$,[2] Ca_3CoRhO_6,[3] and Ca_3CoIrO_6.[4,5] Intriguing quantum phenomena displayed by these materials have recently generated a great deal of interest and discussion (Ref. 5–13 and references therein). The central feature of these systems is the unusually strong correlation between lattice structure and spin-coupling that dictates the magnetism. The spin-chains always comprise alternating face-sharing CoO_6 octahedra and CoO_6 trigonal prisms running along the c-axis. The different crystalline electric fields (CEFs) generate different spin-states for Co ions, leading to chains that have sites with alternating high and low spin-states. The chains form a triangular lattice in the ab-plane that causes geometrical frustration and exotic magnetism. In spite of intensive efforts, understanding these novel phenomena is still a profound challenge, and it is conspicuous that these phenomena have been found exclusively in 3d-based, i.e., Co-based, materials.

In this letter, we report results of structural, magnetic, and specific heat measurements of the newly found single crystal $Sr_5Rh_4O_{12}$. This 4d-based compound features a peculiar crystal structure that favors the formation of spin-chains and a triangular lattice perpendicular to the spin-chains. The crucial results revealed in this work are: (1) geometrical frustration and a partial AFM order at 23 K along the c-axis, and no magnetic anomaly discerned in the ab-plane; (2) a strong FM intrachain coupling and a weak AFM interchain coupling; (3) two steplike transitions in the c-axis isothermal magnetization that lead to a ferrimagnetic state with 1/3 of the saturation moment M_s at a critical field $B^* = 2.4$ T and a fully saturated FM state at $B_c = 4.8$ T. The exotic magnetic behavior displayed by $Sr_5Rh_4O_{12}$ is particularly intriguing because it is the first spin-chain system ever found in 4d and 5d-based materials without a presence of an incomplete 3d-electron shell. It can serve as a model system that offers a rare window into low-dimensional magnetism involving FM chains and geometrically frustrated states.

Refinements of the x-ray diffraction data reveal that $Sr_5Rh_4O_{12}$ has an ordered but inversion twinned trigonal structure with a space group of P3c1 (158) and a mixed valence state of Rh^{3+} and Rh^{4+}. The cell parameters are $a = b = 9.6017(3)$ Å and $c = 21.3105(8)$ Å. The central structural feature is the formation of chains that run along the c-axis and consist of face-sharing RhO_6 octahedra and RhO_6 trigonal prisms as shown in Fig. 1. The RhO_6 trigonal prisms and RhO_6 octahedra alternate along the chains with a sequence of one trigonal prism and three octahedra. The direction of spin-polarization is paralleled to the chains. Of six chains in a unit cell, four chains are distorted similarly; the other two chains related to the Rh11 ion are distorted somewhat differently from the other four. The intrachain Rh–Rh bond for all six chains varies from ∼2.5 to ∼2.7 Å. These uneven Rh–Rh bond distances correlate well with the different ionic sizes of $Rh^{3+}(4d^6)$ and $Rh^{4+}(4d^5)$, which are 0.665 and 0.600 Å, respectively. Accordingly, the sequence of the Rh^{3+} and Rh^{4+} ions in the chains is likely to be Rh^{3+}(o), Rh^{3+}(p), Rh^{4+}(o), and Rh^{4+}(o) where p stands for the RhO_6 trigonal prism, and o for RhO_6 octahedra.

Shown in Fig. 2 is the magnetic susceptibility χ as a function of temperature for (a) the c-axis (χ_c) and the ab-plane (χ_{ab}) at $B = 0.05$ T and (b) χ_c at various fields. The most dominant feature is that the c-axis χ_c shows a sharp peak at $T_N = 23$ K at $B = 0.05$ T, indicating the presence of three-dimensional AFM order, i.e., the spin-chains are primarily AFM coupled with each other. In contrast, the ab-

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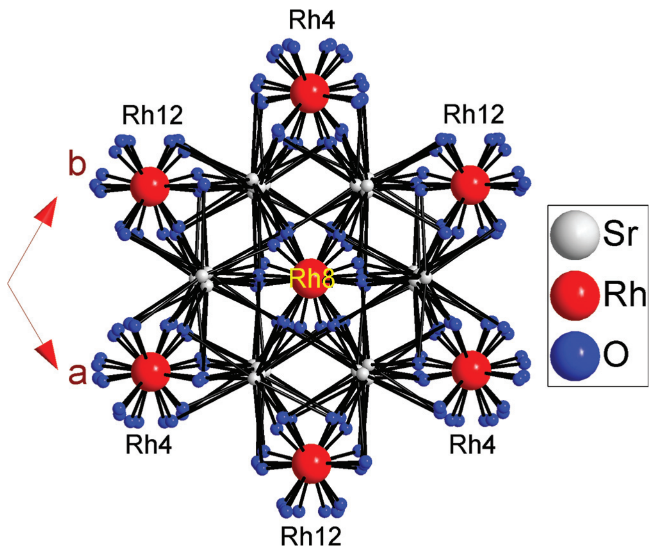

FIG. 1. (Color online) The projection of the crystal structure on the ab-plane, and chain arrays along the c-axis.

plane χ_{ab} displays only a weak temperature dependence, as seen in Fig. 2(a). This large anisotropy underlines the dominant single-ion anisotropy associated with the CEF at the prismatic sites. It is noteworthy that T_N is immediately followed by a shoulder or an anomaly at $T^* = 21.5$ K, which is only visible in low fields. T* accompanies the irreversibility upon in-field and zero-field cooling, which increases with decreasing T. Given the triangular lattice of the spin-chains and the AFM coupling, such behavior may imply the existence of magnetic frustration of spins at $T < T^*$.

A fit of high temperature data of χ_c for $80 < T < 350$ K to a Curie–Weiss law yields an effective moment μ_{eff} of 7.3 μ_B/f.u. and a positive Curie–Weiss temperature θ_{cw} of 28 K (see the inset). Deviations from the Curie–Weiss behavior occur below 45 K. The positive sign of θ_{cw} undoubtedly arises from the ferromagnetic character of the intrachain coupling. The phase transition at T_N can be readily pushed to lower temperatures by increasing B and becomes ill-defined at around $B = 2$ T [see Fig. 2(b)].

Displayed in Fig. 3 is the isothermal magnetization M(B) for (a) the c-axis (M_c) and the ab-plane (M_{ab}) at $T = 1.7$ K and (b) the c-axis M_c at various temperatures. The strong uniaxial anisotropy, a consequence of the Ising character of the spin-coupling, is illustrated as M_{ab} and shows only weak linear field dependence and M_c exhibits two steplike transitions. M_c reveals a few features of the spin-chains. First, for $T < 10$ K, the saturation moment, M_s, reaches 5.30 μ_B/f.u. at a critical

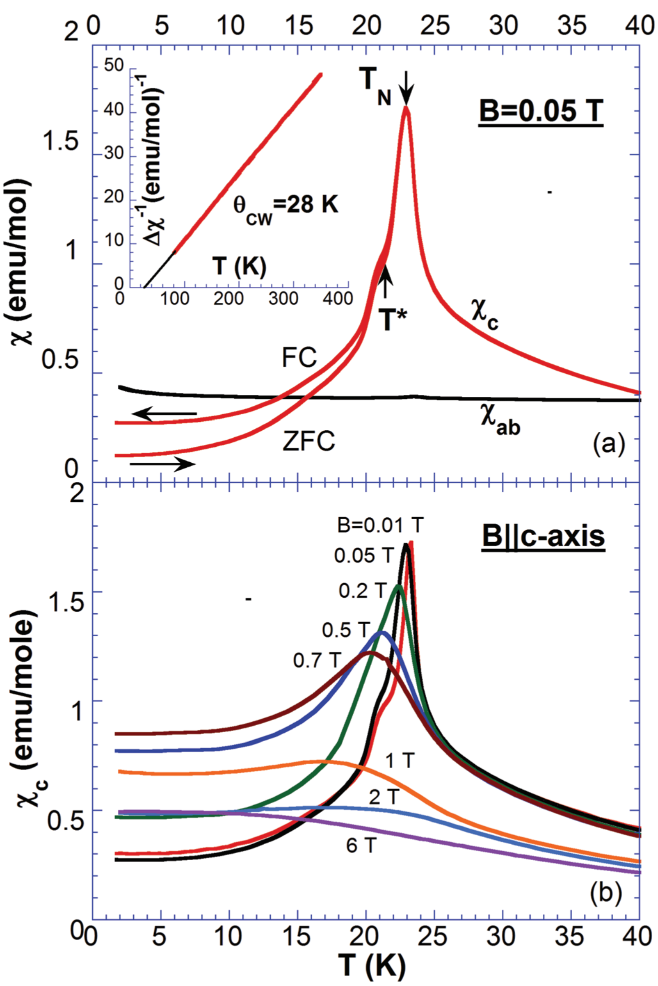

FIG. 2. (Color online) The magnetic susceptibility χ as a function of temperature.

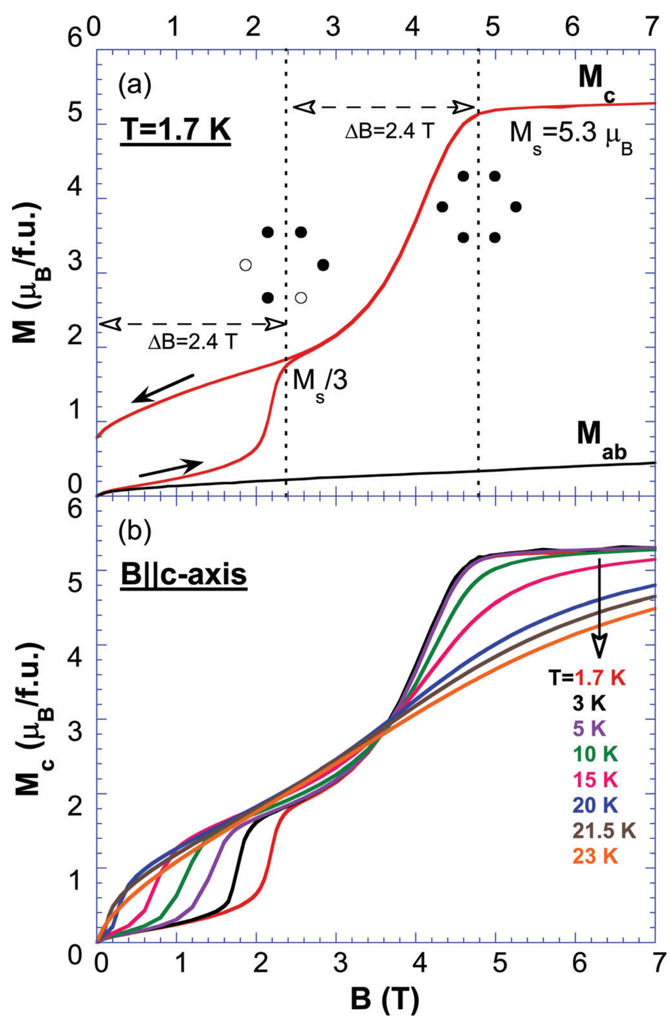

FIG. 3. (Color online) The isothermal magnetization M(B) for the c-axis (M_c) and the ab-plane (M_{ab}).

field $B_c = 4.8$ T. M_s is close but slightly lower than the expected value of 6 μ_B/f.u. for spin-chains with spin-configuration of S = 0, 2, [1/2], and [1/2], assuming a Landé factor g = 2. This discrepancy could be due to the inversion twinning at the Rh11 sites, which results in an average structure that superposes a trigonal prism and an octahedron. Thus, it is possible that the assumed high spin-state at the Rh11 sites may be only partially realized, leading to a moment smaller than 4 μ_B for S = 2. Secondly, M_c at T = 1.7 K rises slightly but visibly at low fields ($B < 0.15$ T) and then undergoes a sharp transition at $B^* = 2.4$ T, reaching 1.73 μ_B/f.u. or about $M_s/3$. After a rapid rise in an interval of 2.4 T, which is interestingly (but probably accidentally) equal to the value of B^*, M_c attains the value M_s at $B_c = 4.8$ T [see Fig. 3(a)]. While the rise in M_c at low fields may be an indication of a slight lifting of degeneracy of the spin-chains, the value of $M_s/3$ at $B^* = 2.4$ T is most likely a sign that the system enters a metamagnetic or ferrimagnetic state that contains FM chains with only 2/3 of them parallel to B and 1/3 antiparallel to B, a situation somewhat similar to that of $Ca_3Co_2O_6$.[2,9] Furthermore, the ferrimagnetic to FM transition at B_c shows no hysteresis, suggesting that it is of second order. In contrast, hysteresis is pronounced below B^* as shown in Fig. 3(a), which is indicative of a first order transition. This effect persists up to 23 K, but weakens as T rises. It reflects the character of a frozen spin-state that prohibits full spin-reversal when B ramps down to zero. No irreversibility would be expected if the magnetic order is purely AFM below B^*. Clearly, this behavior emphasizes the existence of geometrical frustration for $0 \leq B < B^*$. With increasing T, B^* decreases progressively whereas B_c remains unchanged for $T \leq 10$ K and then increases slightly but broadens significantly for $T > 10$ K, as seen in Fig. 3(b). This suggests that the spin–flip process of the spin-chains at B^* is much more sensitive to the thermal energy than that at B_c, as expected for the quenching of the frustration by a field.

Figure 4 illustrates the specific heat C as a function of temperature for $1.8 \leq T \leq 40$ K. It exhibits an anomaly at $T_N \approx 23$ K, where $\Delta C \sim 0.12$ R (the gas constant R = 8.31 J/mol K), confirming the existence of the long-range order at T_N. While the jump in C has the characteristic mean-field in shape, the broadened peak could be the consequence of the nearby second anomaly at $T^* = 21.5$ K immediately below T_N. It is remarkable that ΔC is rather small given the sharp phase transition seen in χ_c. This small value of ΔC is then most likely a signature of the incomplete AFM ordering due to the geometrical frustration, consistent with our magnetic results. The plot of C/T versus T^2 shown in the upper inset displays a linear contribution to C, γT, below 7 K, yielding $\gamma \sim 30$ mJ/mol K^2. Such sizable γ in an insulator arises from the excitations of a frustrated or disordered magnetic state at low T. Similar behavior is observed in disordered insulating magnets[14] and other frustrated systems. As T rises, C/T as a function of T^2 deviates from the linear dependence, implying the emergence of different magnetic excitations (see both insets). These results further emphasize the presence of geometrical frustration due to the triangular lattice of spin-chains at B = 0. A similar behavior is also seen in $Ca_3Co_2O_6$ where $\gamma \sim 10$ mJ/mol K^2.[13] It is noted that the ratio of θ_{cw}/T_N for pyrochlore systems is greater than the partially frustrated systems such as $Ca_3Co_2O_6$.[2,15,16]

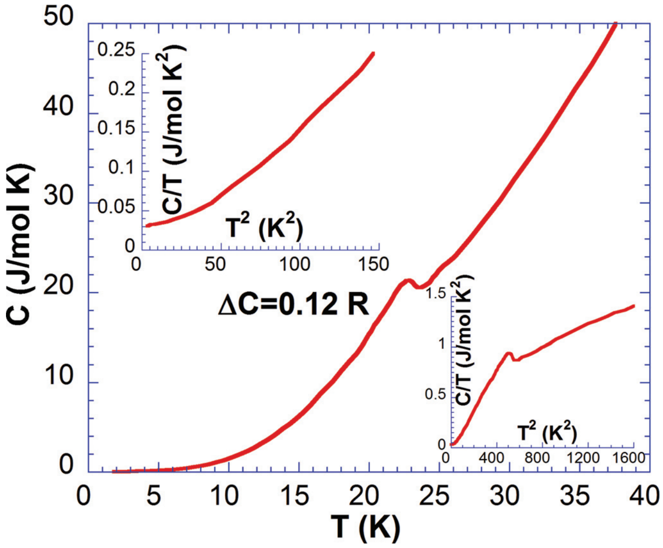

FIG. 4. (Color online) The specific heat C as a function of temperature.

The newly synthesized $Sr_5Rh_4O_{12}$ is the first frustrated Ising-chain system in 4d and 5d-based materials. It shares some common characteristics with Co-based systems, but displays a number of features that are unique.

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[1] M. F. Collins and O. A. Petrenko, Can. J. Phys. **75**, 605 (1997).
[2] A. Aasland *et al.*, Solid State Commun. **101**, 187 (1997).
[3] S. Niitaka *et al.*, J. Solid State Chem. **146**, 137 (1999).
[4] H. Kageyama *et al.*, J. Solid State Chem. **140**, 14 (1998).
[5] S. Rayaprol *et al.*, Phys. Rev. B **67**, 180404(R) (2003).
[6] Y. B. Kudasov, Phys. Rev. Lett. **96**, 027212 (2006).
[7] J. Sugiyama *et al.*, Phys. Rev. Lett. **96**, 197206 (2006).
[8] H. Wu *et al.*, Phys. Rev. Lett. **95**, 186401 (2005).
[9] V. Hardy *et al.*, Phys. Rev. B **70**, 064424 (2004).
[10] S. Niitaka *et al.*, Phys. Rev Lett. **87**, 177202 (2001).
[11] J. Sugiyama *et al.*, Phys. Rev. B **72**, 064418 (2005).
[12] G. Cao *et al.*, New J. Phys. **6**, 159 (2004).
[13] V. Hardy *et al.*, Phys. Rev. B **68**, 014424 (2003).
[14] G. Cao *et al.*, Phys. Rev. B **63**, 144427 (2001).
[15] P. Schiffer and A. P. Ramirez, Comments Condens. Matter Phys. **18**, 21 (1996).
[16] A. P. Ramirez, Annu. Rev. Mater. Sci. **24**, 453 (1994).